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Supporting information for

Columnar self-assembly of rhomboid macrocyclic molecules via step-like intermolecular interaction. Crystal formation and gelation

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Table of Contents

1 Experimental 1
- 1-1 General
- 1-2 Synthesis
- 1-3 Gelation of **1** by ultrasound

2 IR spectra of powder of **1** and xerogel of **1** 3

3 Crystallographically parameters 8

4 Computational Detail 9
- 5-1 Method
- 5-2 Geometries

5 References 18

6 ^{1}H- and ^{13}C{^{1}H}-NMR spectra of all new compounds 19

7 Photophysical properties of **1** and **2** 22
- 7-1 UV-Vis spectra of saturated solution of **1** and xerogel **1**
- 7-2 UV-Vis and fluorescent spectra of **2**

1 Experimental

1-1 General

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (300 MHz) or JEOL JNM-500 spectrometer (500 MHz). The peaks were referenced to residual undeuterated solvents as flows. $CDCl_3$: δ 7.26 for ^{1}H and 77.0 for ^{13}C. THF-d_8: δ 3.58 for ^{1}H and 67.4 for ^{13}C. DMF-d_6: δ 2.74 for ^{1}H. FAB-MS spectra were measured with JEOL JMS-700. Elemental analysis was carried out using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder. The UV-Vis absorption spectra were recorded using JASCO V-530 UV/Vis spectrometer. IR spectra were measured with Shimadzu FTIR-8100A. To prepare KBr pellets, about 1–2 mg of sample were taken, grinded together with about 100 mg of KBr. SEM observations were carried out by Hitachi High-Technologies S-5200. XRD patterns were measured by RIGAKU RINT200. X-ray crystallography was performed on Rigaku Saturn CCD area detector equipped with monochromated Mo Kα radiation (l = 0.71073 Å) at −160 ^{o}C.

1-2 Synthesis

Biphenyl-2,2'-dicarbaldehyde.[1] Phenanthrene (4.02 g, 23 mmol) was dissolved in dichloromethane (50 mL) and methanol (50 mL) at −84 $^{\circ}$ C. Ozone gas was bubbled to the reaction mixture until color of the reaction mixture changed to blue. After the excess ozone was removed by oxygen bubbling, NaI (10.3 g, 69 mmol) and Acetic acid (15 mL) was added and stirred for 1 h at room temperature. The reaction mixture was washed with aqueous 5% $NaHSO_3$ and brine and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Recrystallization from diethyl ether/hexane gave pale yellow crystal (3.06 g, 65%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.84 (s, 2H, CHO), 8.07 (d, 2H, H3 and H3'), 7.64 (sextet,4H, H4, H5, H4' and H5'), 7.36 (d, 2H, H6 and H6').

^{13}C-NMR (75 Hz, $CDCl_3$): δ 191.03, 141.20, 134.55, 133.42, 131.70, 128.82, 128.55.

IR (KBr): 3080, 2834, 2749, 1694, 1592, 1392, 1195, 821, 763, 650, 439 cm^{-1}.

1,3-Bis(4-aminophenylethyny)benzene. $PdCl_2(PPh_3)_2$ (84.8 mg, 0.12 mmol), CuI (18.0 mg, 0.01 mmol), 4-ethynylaniline (0.562 g, 4.8 mmol), 0.5 mM aqueous ethanolamine (12 mL), THF (12 mL), and 1,3-dibromobenzene (0.24 mL, 2.0 mmol) were placed in Schlenk tube under argon. The mixture was heated at 60 $^{\circ}$ C for 26 h. The reaction mixture was washed with water and brine, and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, dichloromethane/hexane 4:1) to afford pale yellow solid (528 mg, 86%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.63 (m, 1H, 2-CC_6H_4C), 7.40 (d, 2H, 4,6-CC_6H_4C), 7.34 (d, 4H, *meta*-$NH_2C_6H_4C$), 7.28 (t, 2H, 5-CC_6H_4C), 6.64 (d, 4H, *ortho*-$NH_2C_6H_4$), 3.8 (br. s, 4H, NH_2).

^{13}C-NMR (75 Hz, $CDCl_3$): δ 146.71, 134.07, 133.00, 130.43, 128.27, 124.11, 114.73, 112.44, 90.54, 86.71.

IR (KBr): 3729, 3445, 3411, 3327, 3219, 3035, 2193, 1633, 1603, 1583, 1510, 1303, 1267, 1177, 902, 834, 823, 802, 691, 602, 531, 508, 492 cm^{-1}.

Anal. Calcd for $C_{22}H_{16}N_2\cdot(H_2O)_{0.1}$: C, 85.19; H, 5.26, N, 9.03. Found: C 85.12; H, 5.26; N, 9.03.

Macrocycle 1. Biphenyl-2,2'-dicarbaldehyde (21.1 mg, 0.10 mmol), 1,3-bis(4-aminophenylethynyl) benzene (30.7 mg, 0.10 mmol), and TsOH·H_2O (0.6 mg, 3 □mol) were dissolved in acetonitrile (20 mL). The solution was stirred at 0 ° C for 24 h. The reaction mixture was filtered and residual solid was washed with THF to afford a yellow solid of **1** (47.9 mg, 92%).

^{1}H-NMR (300 MHz, DMF-d_7): δ 8.28 (s, 4H, NCH), 8.26 (m, 4H, biphenyl-6,6') 8.7–7.4 (m, 28H, 4,5-NCHC$_6H_4$ and 2-CC$_6$H$_4$C), 7.12 (d, 8H, ortho-NC$_6$H$_4$).

MS (FAB, 2-nitrophyenyl n-octyl ether/N-methylpyrrolidone): m/z = 965 (M + H$^+$).

IR (KBr): 1620, 1585, 1500, 1190, 889, 835, 792, 758, 684, 617, 549 cm^{-1}. Anal. Calcd for $C_{72}H_{44}N_4$·(THF)1.5: C, 87.29; H, 5.26, N, 5.22, Found: C, 87.21; H, 5.15; N, 5.19.

Macrocycle 2. **1** (40.8 mg, 0.042 mmol) and Zn(Cu) (83.2 mg, 1.2 mmol) were dispersed in DMF (2 mL) under argon atmosphere. The mixture was heated at 60 °C for 24 h. After the reaction mixture was cooled down to room temperature, TsOH·H_2O (573 mg, 3.0 mmol) in water (1 mL) was added and stirred for 40 min at room temperature. The reaction mixture was washed with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2/0.5% triethylamine), and washed with a small amount of MeCN to afford **2** as pale yellow powder (18.8 mg, 46%). Single crystals suited for X-ray crystallography were obtained by vapor diffusion of cyclohexane to a $CHCl_3$ solution of **2**.

^{1}H-NMR (300 MHz, THF-d_8): □ 7.98 (d, 4H, Ar), 7.64 (s, 2H, Ar), 7.5–7.2 (m, 28H, Ar), 6.78 (d, 8H, Ar), 5.44 (d, 4H, NH), 4.93 (d, 4H, dihydrophenanthrene-9,10).

^{13}C-NMR (75 Hz, THF-d8, r. t.): □ 148.93, 137.28, 135.96, 134.50, 133.98, 133.77, 131.77,130.07, 129.47, 129.15, 125.73, 124.54, 113.47, 111.29, 92.29, 87.18, 55.85.

MS (FAB, 3-nitrobenzyl alcohol): m/z = 969 (M + H+).

IR (KBr): 2201, 1608, 1587, 1516, 1246, 1182, 821, 736, 686 cm^{-1}.

Anal. Calcd for $C_{72}H_{48}N_4$·$(THF)_{1.5}$: C, 86.96; H, 5.61, N, 5.20, Found: C, 87.13; H, 5.30; N, 5.15.

1-3 Gelation of 1 by ultrasound

1 (3 mg) and solvents (0.2 mL) were placed in a vial and sealed. The mixture was irradiated ultrasound for 1 min or 20 min. And then standing for ca. 30 min. Ultrasound was generated by ultrasonic cleaner (LEO-80, 56 mW cm^{-2}, 46 kHz). The gel formation was evaluated by "stable to inversion of a test tube" method.

2 IR spectra of powder of 1 and xerogel of 1

Powder of **1** and xerogel of **1** shows peak around 1620 cm^{-1} assigned to imine bond (Figure S1–S6 and Table S1). This result supported by DFT computation at B97-D/TZVP level of theory (Figure S7). On the other hand, polymerized side product shows peak at 1674 cm^{-1} assigned to aldehyde (Figure S6). This results also supported by DFT computation of model compound that shows peak at 1700 cm^{-1} due to aldehyde (Figure S8). These results indicated that chemical reaction didn't occur by ultrasound irradiation.

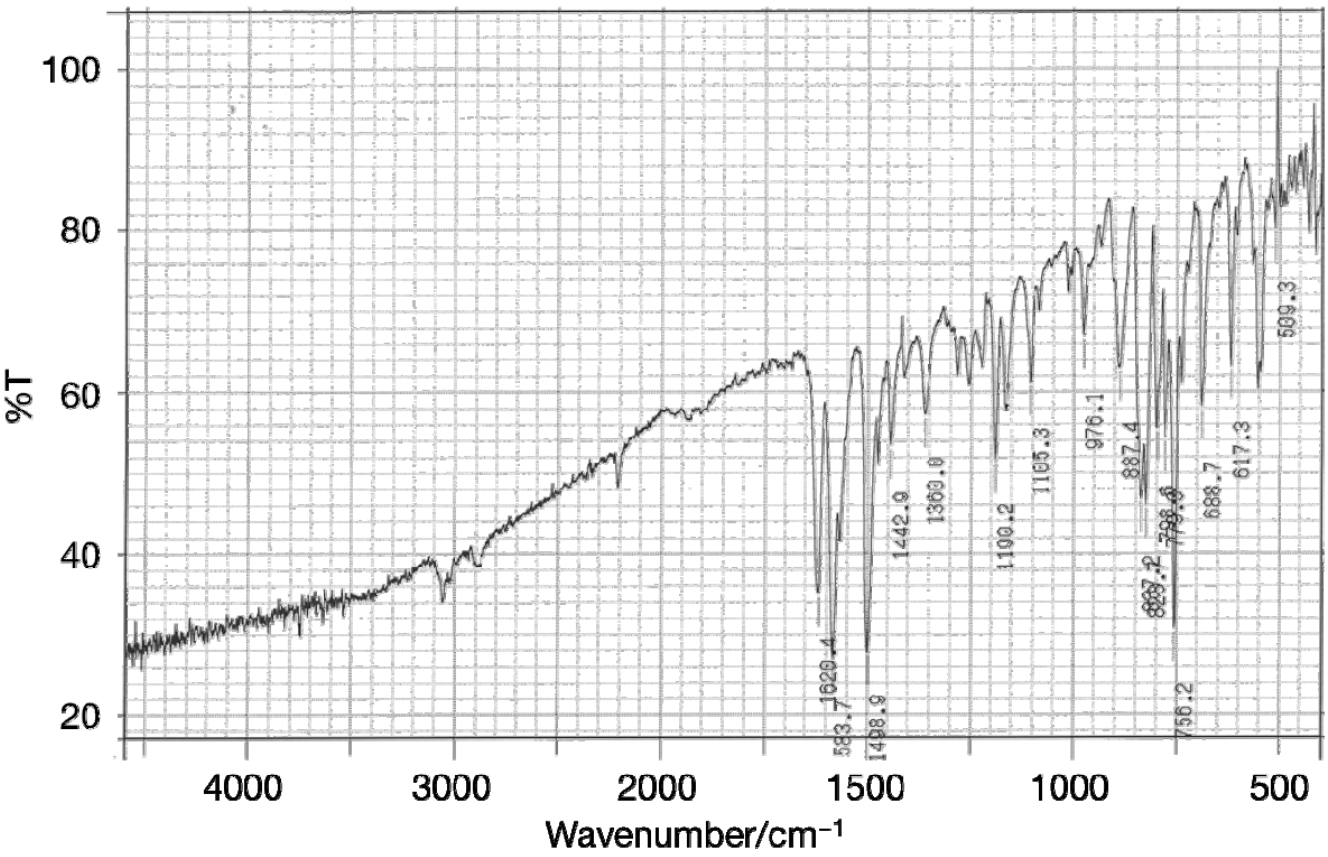

Figure S1. IR spectrum of powder of **1** before ultrasound irradiation.

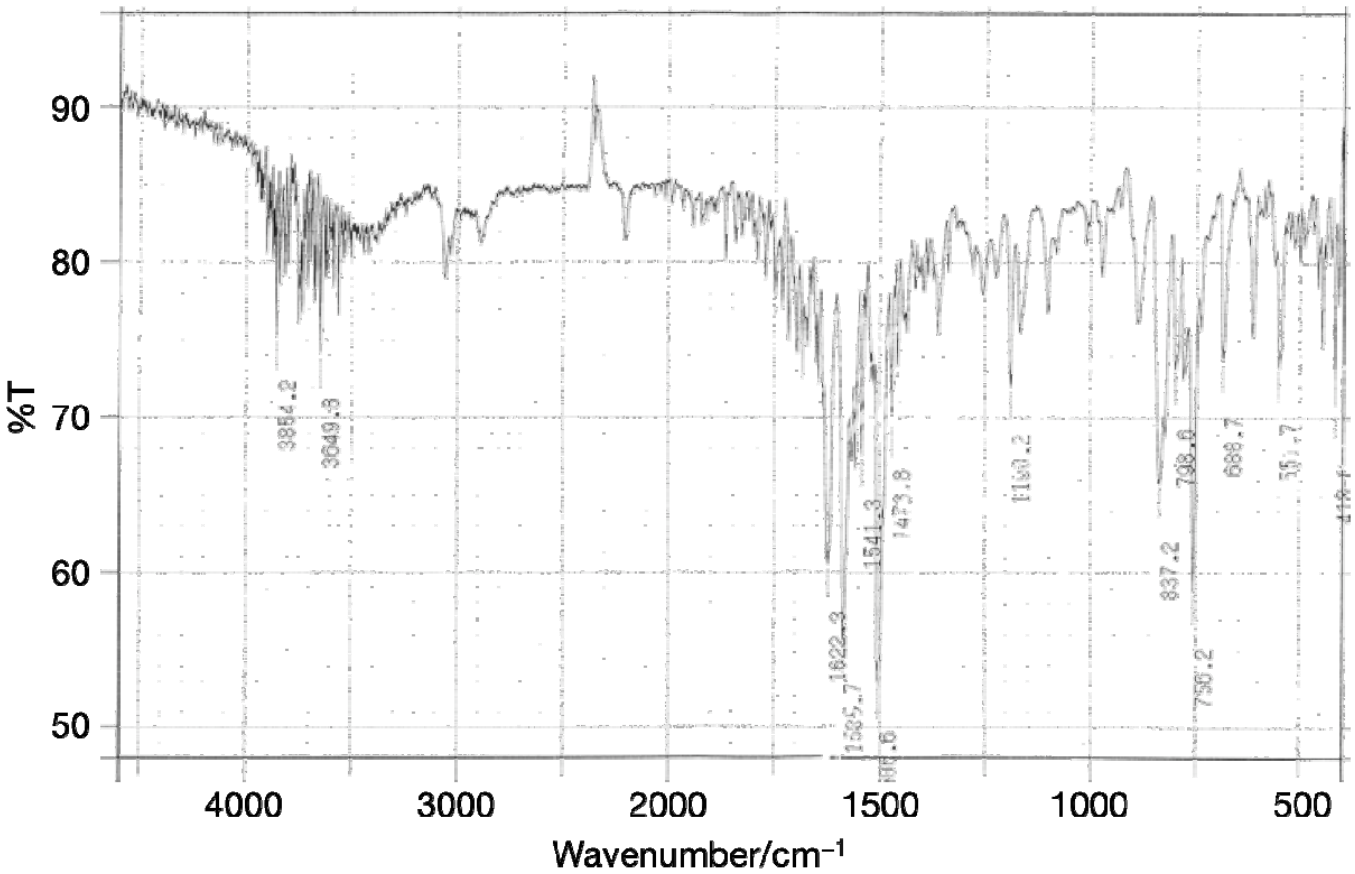

Figure S2. IR spectrum of xerogel of **1** prepared in DMF.

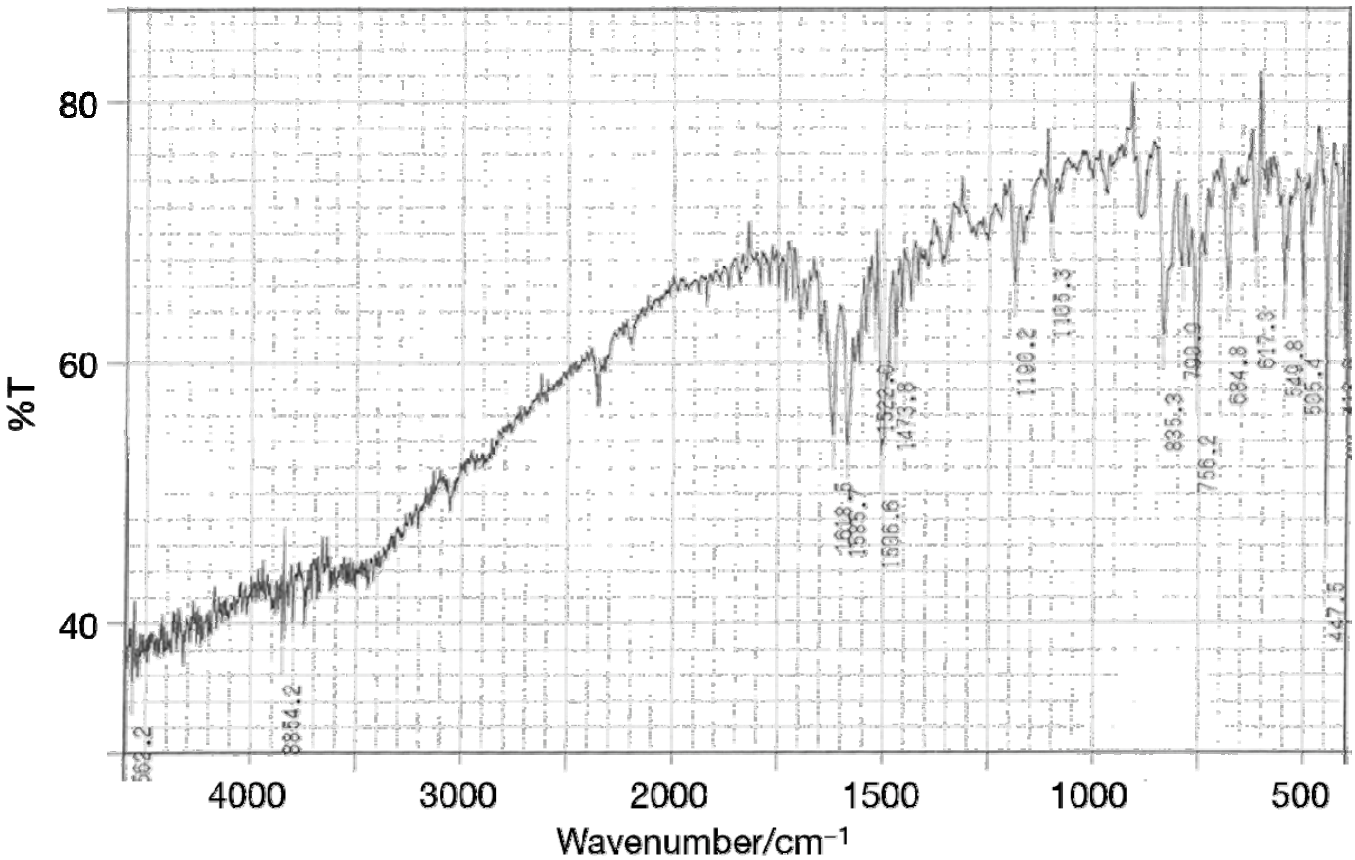

Figure S3. IR spectrum of xerogel of **1** prepared in DMAc.

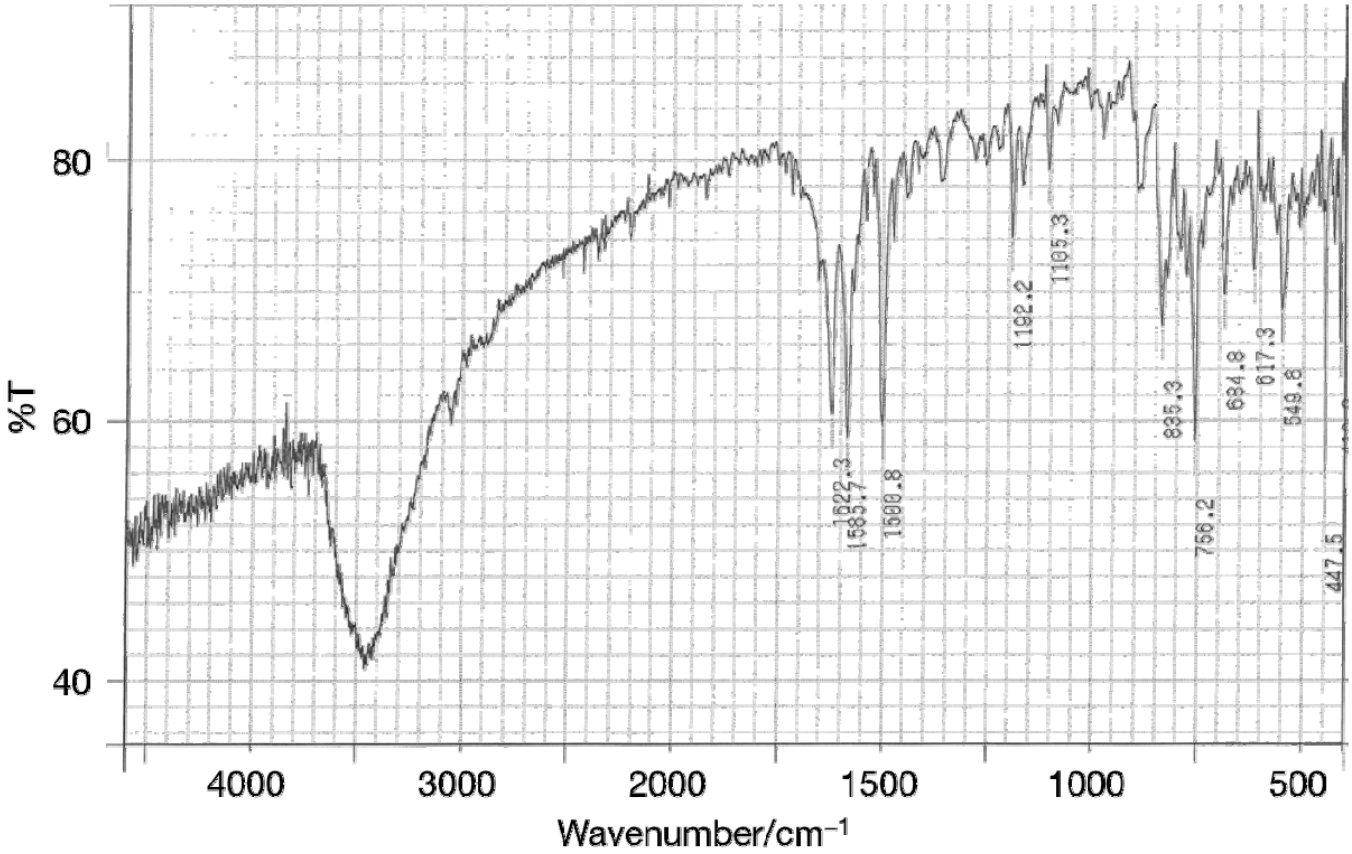

Figure S4. IR spectrum of xerogel of **1** prepared in CH_2Cl_2.

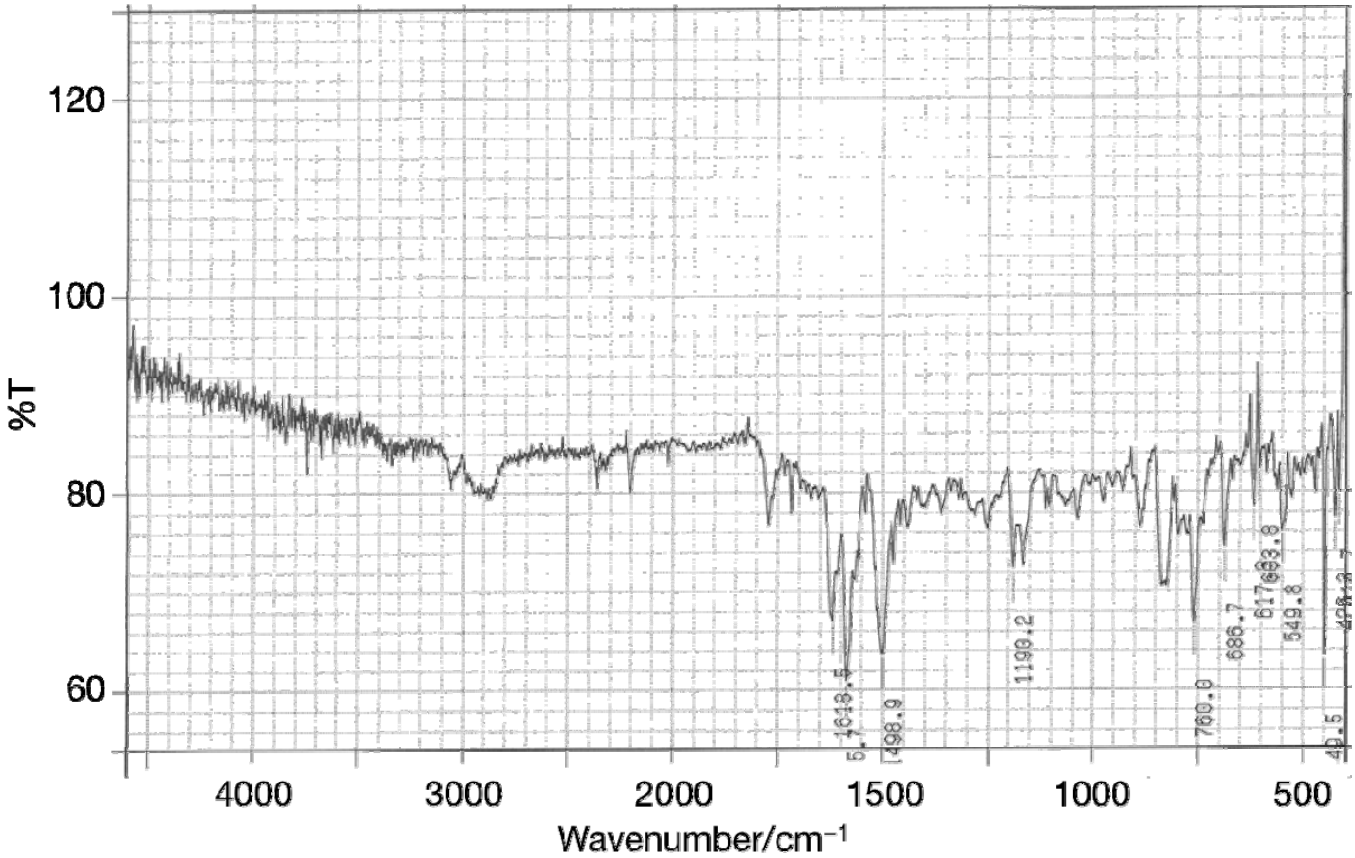

Figure S5. IR spectrum of xerogel of **1** prepared in THF.

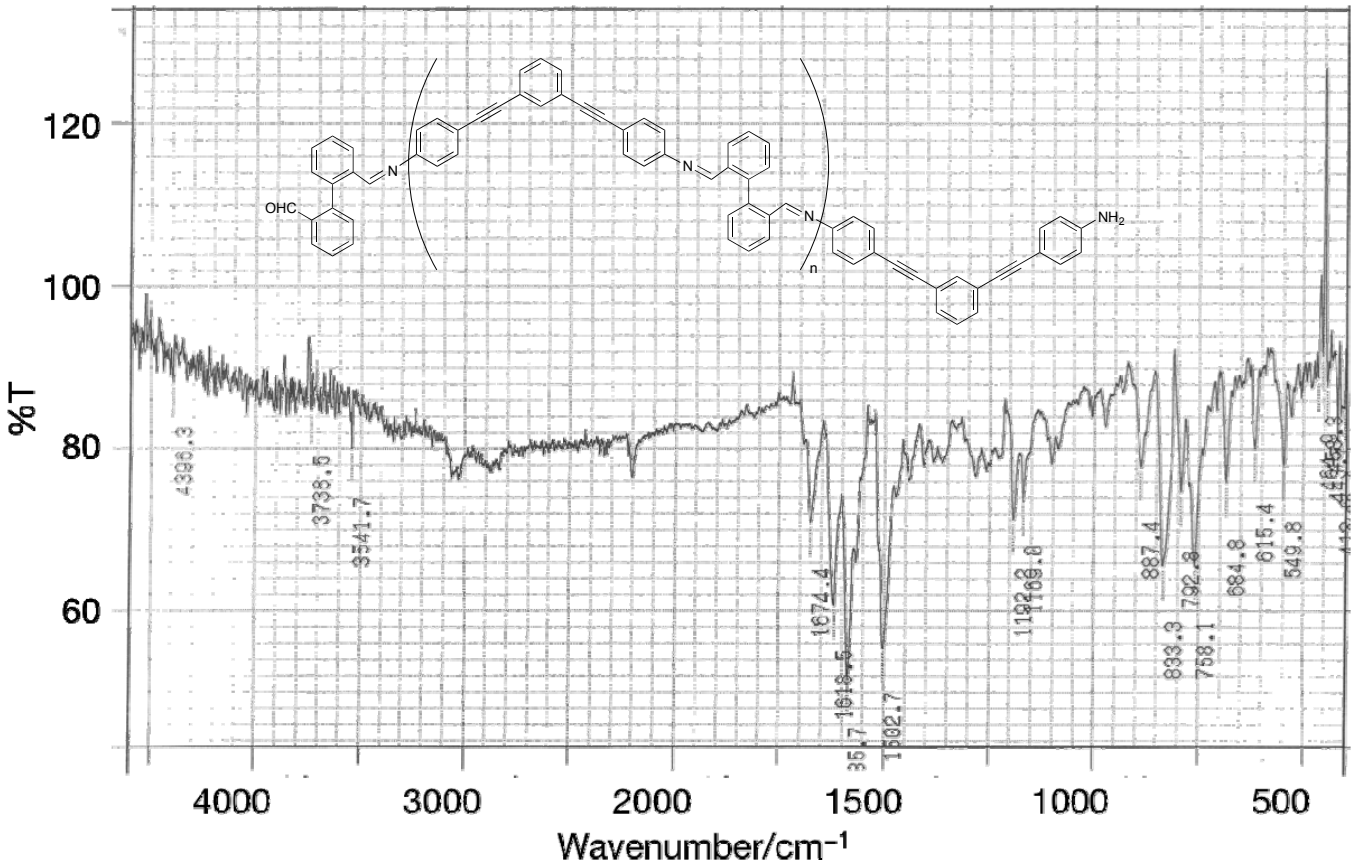

Figure S6. IR spectrum of polymer (side product).

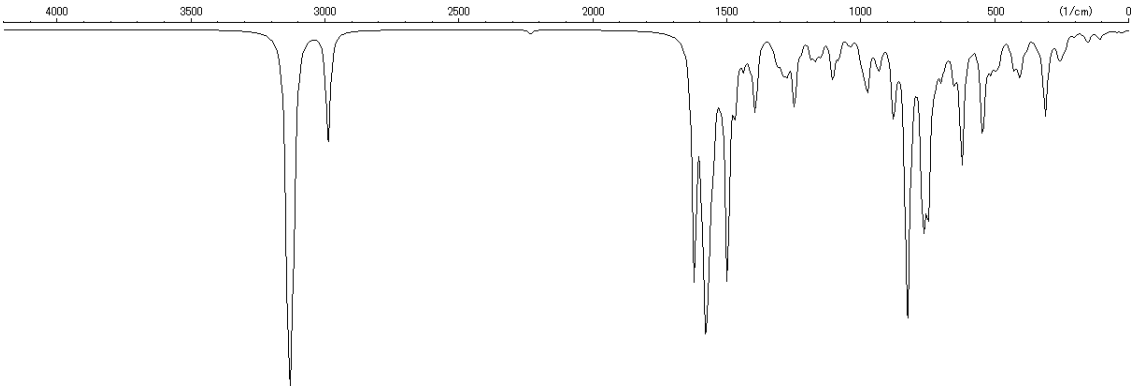

Figure S7. Estimated IR spectrum of **1** (B97-D/TZVP) drawn by Winmostar[2].

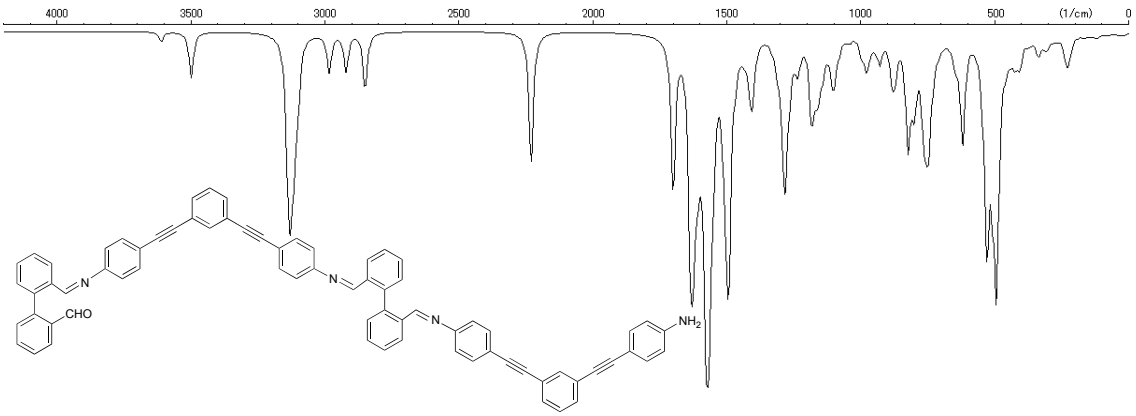

Figure S8. Estimated IR spectrum of precursor of **1** (B97-D/TZVP) drawn by Winmostar[2].

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Table S1. Assignment of IR spectra.

Sample	Wavenumber/cm^{-1}	Assignment
Before ultrasonification	1620	C=N
Xerogel (DMF)	1622	C=N
Xerogel (DMAc)	1619	C=N
Xerogel (DCM)	1622	C=N
Xerogel (THF)	1619	C=N
Polymer (side product)	1674	C=O
	1618	C=N
1 (B97-D/TZVP)	1621	C=N
Precursor of **1** (B97-D/TZVP)	1700	C=O
	1635	NH_2
	1622,1629	C=N

3 Crystallographically parameters.

Crystallographically parameters of **2** were summarized in Table S2.

Table S2. Crystallographically parameters.

	2·2CyH
Formula	$C_{90}H_{84}N_4$
F_w	1221.68
Size of crystal/mm	0.80 x 0.20 x 0.20
Crystal System	monoclinic
Space Group	$P2_1/n$ (no. 14)
a/Å	9.424(14)
b/Å	17.14(3)
c/Å	23.45(4)
α/°	-
β/°	91.541(18)
γ/°	-
V/Å^3	3786(10)
Z	2
D_c/g cm^{-3}	1.072
No. of reflections measured	31070
No. of unique reflections	8020
No. of observations ($I > 2.0\sigma(I)$)	1709
R ($I > 2.0\sigma(I)$)	0.1181
R_w ($I > 2.0\sigma(I)$)	0.2957
Goodness of fit	1.001

4 Computational detail

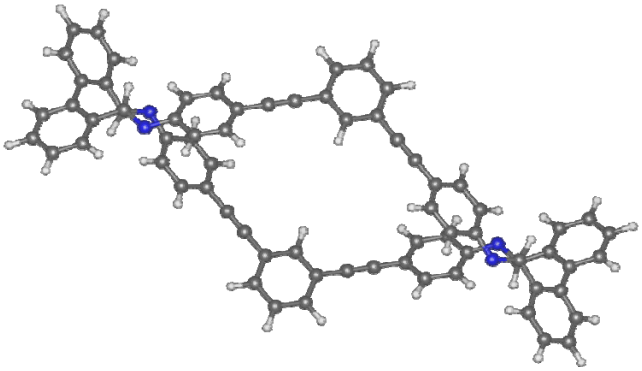
4-1 Method

All calculation have been performed with Gaussian 09, revision B.01.[3] Geometry optimization was performed by semi-empirical dispersion corrected B97-D functional[4] with the Ahlrichs's TZVP basis set.[5] For accretion of the DFT calculations, the density fitting (also known as the resolution of identity (RI) approximation) for the two-electron integrals[6] was applied with the TZVPFit auxiliary basis set[6a, 7] that implemented in Gaussian 09. All optimized structures were verified to be local minima by hessian calculation. Since DFT-D method is insensitive to basis set superposition errors,[4] interaction energy dose not include counterpoise correction.

4-2 Geometries

B97-D/TZVP optimized geometries, energy, and number of imaginary frequencies of the macrocycle **1**, precursor of **1**, benzene-diphenylethyne π–π complex, benzene-benzene parallel-displaced stacking π–π complex, diphenylethyne and benzene are show in following list.

Macrocycle 1



C	-0.93702	-3.89319	-1.29445
C	0.46388	-3.95365	-1.52197
C	-1.65328	-2.70554	-1.54430
C	-1.62600	-5.01743	-0.78100
C	-2.99470	-4.94238	-0.52222
C	-3.03324	-2.62498	-1.27008
C	-3.70060	-3.76232	-0.75696
H	-1.07493	-5.93455	-0.58898
H	-3.51649	-5.81241	-0.12834
H	-1.13100	-1.83478	-1.93055
C	-3.74035	-1.40969	-1.47282
H	-4.76530	-3.70191	-0.54620
C	1.67306	-4.00496	-1.67481
C	3.08432	-4.06297	-1.79471
C	-4.34850	-0.36040	-1.60407
C	-5.05486	0.86501	-1.69856
C	-6.14881	1.12477	-0.83862
C	-4.66045	1.87351	-2.60900
C	-5.32182	3.09448	-2.63835
C	-6.81462	2.34093	-0.87913
C	-6.41290	3.35103	-1.78254
H	-3.81593	1.69108	-3.26902

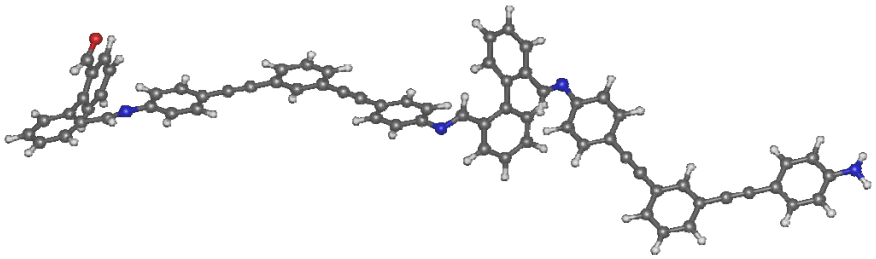
H	-5.00085	3.88276	-3.31554
H	-6.44374	0.36817	-0.11544
H	-7.60349	2.53565	-0.15851
N	-6.95353	4.64305	-1.80778
C	3.78055	-3.23239	-2.70408
C	3.83501	-4.92666	-0.96147
C	5.22030	-4.95437	-1.02668
C	5.16820	-3.25426	-2.75821
C	5.91460	-4.11709	-1.92934
H	3.31294	-5.54950	-0.23903
H	5.76991	-5.57533	-0.32535
H	3.21715	-2.55719	-3.34346
H	5.70718	-2.59449	-3.43438
N	7.30963	-3.99928	-1.97751
C	-8.13554	4.88422	-1.36015
H	-8.80922	4.08529	-1.02120
C	-8.64918	6.25689	-1.24724
C	8.07702	-4.94330	-1.55851
H	7.68537	-5.91538	-1.22898
C	9.53352	-4.76652	-1.46842
C	10.17519	-3.80388	-2.27321
C	10.31059	-5.56295	-0.58389
C	11.70557	-5.38717	-0.56672
C	11.55655	-3.64085	-2.23473
C	12.32773	-4.44053	-1.38080
C	9.71026	-6.56903	0.33542
H	12.29837	-5.98787	0.11999
H	9.55894	-3.20385	-2.93775
H	12.03480	-2.89883	-2.87097
H	13.40865	-4.32033	-1.34305
C	-9.69861	6.57003	-0.34095
C	-8.10572	7.27844	-2.05183
C	-8.59741	8.57872	-1.99157
C	-10.18573	7.88849	-0.30199
C	-9.64721	8.88543	-1.11563
H	-7.30122	7.01525	-2.73367
H	-8.17102	9.35169	-2.62783
C	-10.29894	5.56395	0.57836
H	-10.98001	8.13026	0.40120
H	-10.03837	9.89946	-1.06072
C	-11.69392	5.38817	0.56119
C	-9.52187	4.76752	1.46288
C	-10.16353	3.80487	2.26767
C	-12.31607	4.44152	1.37527
C	-11.54489	3.64184	2.22920
C	-8.06536	4.94430	1.55296
H	-9.54728	3.20485	2.93220
H	-12.28672	5.98886	-0.12552
H	-13.39700	4.32132	1.33753
H	-12.02314	2.89982	2.86544
C	8.66081	-6.25588	1.24170
C	10.19736	-7.88749	0.29646
C	9.65884	-8.88443	1.11010
C	8.11735	-7.27742	2.04630

C	8.60904	-8.57771	1.98604
H	10.99165	-8.12926	-0.40673
H	10.04999	-9.89846	1.05520
C	8.14718	-4.88320	1.35461
H	7.31285	-7.01423	2.72813
H	8.18264	-9.35067	2.62230
H	-7.67372	5.91638	1.22344
N	-7.29797	4.00028	1.97196
C	-5.90294	4.11810	1.92378
H	8.82087	-4.08428	1.01565
N	6.96517	-4.64203	1.80222
C	6.42455	-3.35000	1.77698
C	-5.15654	3.25526	2.75264
C	-5.20864	4.95539	1.02112
C	-3.82335	4.92768	0.95591
C	-3.76889	3.23339	2.69850
C	-3.07267	4.06398	1.78914
H	-5.75826	5.57636	0.31980
H	-3.30130	5.55054	0.23347
H	-5.69551	2.59548	3.42880
H	-3.20548	2.55818	3.33787
C	-1.66140	4.00598	1.66923
C	6.82627	-2.33992	0.87356
C	5.33347	-3.09345	2.63278
C	4.67211	-1.87248	2.60344
C	6.16047	-1.12375	0.83305
C	5.06652	-0.86398	1.69299
H	5.01250	-3.88172	3.30998
H	3.82758	-1.69004	3.26345
H	7.61514	-2.53464	0.15295
H	6.45540	-0.36716	0.10986
C	4.36017	0.36143	1.59849
C	-0.45223	3.95467	1.51638
C	3.75201	1.41072	1.46723
C	3.04490	2.62600	1.26449
C	3.71225	3.76335	0.75137
C	1.66494	2.70656	1.53871
C	0.94868	3.89421	1.28886
C	3.00635	4.94341	0.51663
C	1.63766	5.01846	0.77541
H	1.14266	1.83581	1.92496
H	4.77696	3.70293	0.54061
H	3.52815	5.81344	0.12275
H	1.08658	5.93558	0.58339

Energy = −2987.62443142 hartree

Number of imaginary frequencies = 0

Precursor of 1



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C	2.28690	-6.66118	-7.02923
C	2.74051	-6.22828	-8.26816
C	3.15148	-4.88665	-8.46015
C	3.08815	-4.00085	-7.35795
C	2.65396	-4.44264	-6.11453
C	3.59656	-4.43676	-9.72785
C	3.98280	-4.05163	-10.81925
C	4.43335	-3.60052	-12.08795
C	4.50262	-4.49255	-13.17682
C	4.94889	-4.05812	-14.44161
C	5.32879	-2.70406	-14.60452
C	5.26022	-1.82055	-13.52699
C	4.81880	-2.25189	-12.27583
C	5.01543	-4.96486	-15.53144
C	5.07343	-5.74348	-16.46937
C	5.14016	-6.64839	-17.55762
C	5.59153	-6.22855	-18.83119
C	5.65888	-7.11555	-19.89774
C	5.28121	-8.46532	-19.73787
C	4.82673	-8.89092	-18.47202
C	4.75993	-8.00287	-17.40633
C	2.28792	-5.85257	-3.59674
C	1.77402	-6.26466	-2.28598
C	0.58439	-7.01879	-2.19274
C	0.04949	-7.36411	-0.95682
C	0.69269	-6.95595	0.22046
C	1.87129	-6.21376	0.14587
C	2.43324	-5.86514	-1.09390
C	3.72936	-5.12858	-1.11182
C	4.85964	-5.76395	-1.65334
C	6.10981	-5.14565	-1.64141
C	6.25070	-3.86702	-1.08322
C	5.14158	-3.21773	-0.55320
C	3.86845	-3.82757	-0.56101
C	-6.72051	7.46815	13.94763
H	1.96014	-7.68834	-6.88441
H	2.77228	-6.91568	-9.11008
H	3.37653	-2.96160	-7.49806
H	2.58662	-3.74214	-5.28490
H	4.20808	-5.52925	-13.03968
H	5.67324	-2.36398	-15.57789
H	5.55469	-0.78183	-13.66442

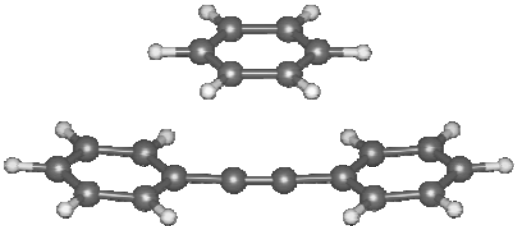
H	4.76596	-1.56209	-11.43742
H	5.89039	-5.19231	-18.97087
H	6.00745	-6.76924	-20.86997
H	4.52650	-9.92876	-18.33269
H	4.41099	-8.34863	-16.43614
H	3.12687	-5.14251	-3.58614
H	0.09269	-7.31055	-3.11731
H	-0.86976	-7.94405	-0.90468
H	0.27856	-7.21831	1.19199
H	2.38203	-5.90721	1.05622
H	4.74792	-6.76161	-2.07251
H	6.97185	-5.65922	-2.06250
H	7.22381	-3.38024	-1.07041
H	5.22551	-2.21944	-0.13118
N	-4.47684	8.25190	11.59157
N	2.79245	-1.97165	0.55266
C	-4.59709	7.54268	10.39588
C	-3.49013	6.78240	9.96401
C	-3.55008	6.05016	8.78654
C	-4.73794	6.01558	8.01524
C	-5.85994	6.74568	8.47396
C	-5.78979	7.49800	9.63987
C	-4.80735	5.25053	6.82473
C	-4.86306	4.59303	5.79854
C	-4.92901	3.82888	4.60403
C	-3.81039	3.09040	4.16858
C	-3.86387	2.32892	2.98387
C	-5.06153	2.31350	2.22999
C	-6.16933	3.04396	2.66066
C	-6.11579	3.79733	3.83361
C	-2.73099	1.58820	2.55581
C	-1.75814	0.95059	2.18772
C	-0.62764	0.20830	1.76510
C	0.56609	0.20692	2.52708
C	1.67876	-0.50589	2.10084
C	1.63548	-1.27598	0.91973
C	0.45141	-1.26298	0.14766
C	-0.65702	-0.53462	0.56078
C	-5.04523	9.39334	11.73769
C	-5.03364	10.16526	12.98562
C	-5.37487	11.52914	12.88352
C	-5.33483	12.37821	13.98791
C	-4.95371	11.86608	15.23098
C	-4.63585	10.50986	15.35636
C	-4.68208	9.63827	14.25914
C	-4.36574	8.20027	14.50121
C	-3.07397	7.86275	14.92948
C	-2.72279	6.53276	15.17234
C	-3.66545	5.51160	14.99944
C	-4.95808	5.83414	14.59514
C	-5.32421	7.16858	14.35128
C	2.69742	-3.10084	-0.05890
H	-2.58506	6.79639	10.56666
H	-2.68642	5.48080	8.45155

H	-6.78692	6.70275	7.90699
H	-6.67022	8.02494	10.00096
H	-2.89519	3.10833	4.75365
H	-5.10562	1.72710	1.31578
H	-7.08619	3.02576	2.07475
H	-6.98032	4.36544	4.16740
H	0.60543	0.78369	3.44803
H	2.59952	-0.49812	2.67955
H	0.42106	-1.80683	-0.79400
H	-1.55916	-0.52166	-0.04650
H	-5.55234	9.89255	10.89283
H	-5.65742	11.92229	11.90764
H	-5.59638	13.42854	13.87968
H	-4.91628	12.51341	16.10483
H	-4.36840	10.10407	16.32992
H	-2.33386	8.65197	15.04460
H	-1.71044	6.29337	15.49312
H	-3.39138	4.47504	15.18469
H	-5.71654	5.06542	14.46441
H	1.72186	-3.57706	-0.23088
H	5.90103	-9.08957	-21.58854
H	5.32109	-10.32573	-20.59578
O	-7.56718	6.62591	13.69531
H	-6.97360	8.54992	13.89227

Energy = −3064.03911302 hartree

Number of imaginary frequencies = 0

Benzene-diphenylethyne π–π complex



C	-1.30279	0.12826	0.20011
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C	2.44507	1.06036	-0.30158
C	1.68183	1.59919	-1.34302
C	1.12990	0.75802	-2.31461
C	1.34419	-0.62239	-2.24506
C	2.10758	-1.16122	-1.20371
H	3.23336	-0.74134	0.59069
H	2.86556	1.71363	0.46098
H	2.26562	-2.23660	-1.14314
H	0.51902	1.17493	-3.11254
H	1.50704	2.67253	-1.39240
H	0.90714	-1.27769	-2.99651
C	-0.63985	-0.34813	1.10449

C	0.18823	-0.89593	2.11677
C	-2.01587	0.68829	-0.89000
C	-2.52889	-0.13880	-1.91494
C	-2.19031	2.08707	-0.99368
C	-2.85067	2.63628	-2.09196
C	-3.18780	0.42003	-3.00919
C	-3.35077	1.80787	-3.10453
H	-1.79324	2.72781	-0.21014
H	-2.97545	3.71541	-2.16032
H	-2.39249	-1.21501	-1.84209
H	-3.57534	-0.22862	-3.79265
H	-3.86449	2.24038	-3.96073
C	0.79992	-0.05908	3.07765
C	0.45089	-2.28414	2.15830
C	1.30363	-2.81227	3.12666
C	1.65118	-0.59686	4.04203
C	1.90856	-1.97331	4.07107
H	-0.01336	-2.93127	1.41815
H	1.49921	-3.88287	3.14519
H	0.60485	1.01010	3.04668
H	2.11773	0.05969	4.77418
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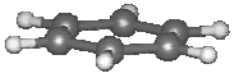
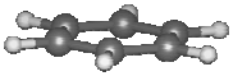
Energy = −771.3675625 hartree

Number of imaginary frequencies = 0

Benzene-benzene parallel-displaced stacking π–π complex





C	0.70326	0.99212	0.14479
H	1.36125	1.84179	0.31384
C	1.23286	-0.30046	0.09298
H	2.30160	-0.45507	0.22385
C	0.38567	-1.39584	-0.10595
H	0.79792	-2.40281	-0.13976
C	-0.99179	-1.19897	-0.25117
H	-1.65108	-2.05176	-0.40437
C	-1.52219	0.09558	-0.19900
H	-2.59399	0.24994	-0.31222

C	-0.67388	1.19070	-0.00269
H	-1.08631	2.19722	0.04252
C	2.03039	1.19854	3.85969
H	2.68992	2.05127	4.01213
C	2.56059	-0.09608	3.80710
H	3.63248	-0.25055	3.91923
C	1.71195	-1.19112	3.61176
H	2.12422	-2.19769	3.56621
C	0.33468	-0.99240	3.46567
H	-0.32357	-1.84201	3.29738
C	-0.19472	0.30025	3.51790
H	-1.26358	0.45497	3.38814
C	0.65280	1.39555	3.71585
H	0.24069	2.40257	3.75000

Energy = −464.295329798 hartree

Number of imaginary frequencies = 0

Diphenylethyne

C	-2.02981	0.00000	0.00000
C	-0.60977	0.00000	0.00000
C	-2.75049	1.21694	0.00052
C	-2.75049	-1.21694	-0.00052
C	-4.14481	-1.21108	-0.00052
C	-4.14482	1.21108	0.00052
C	-4.84797	-0.00000	0.00000
H	-2.20235	-2.15609	-0.00093
H	-4.68622	-2.15524	-0.00093
H	-2.20235	2.15610	0.00093
H	-4.68622	2.15523	0.00093
H	-5.93609	-0.00000	0.00000
C	0.60977	0.00000	0.00000
C	2.02981	0.00000	0.00000
C	2.75049	-1.21694	-0.00057
C	2.75049	1.21694	0.00057
C	4.14482	1.21108	0.00057
C	4.14481	-1.21108	-0.00057
C	4.84797	-0.00000	0.00000
H	2.20235	2.15610	0.00101
H	4.68622	2.15523	0.00101
H	2.20235	-2.15609	-0.00101
H	4.68622	-2.15524	-0.00101

H	5.93609	-0.00000	0.00000

Energy = −539.215054746 hartree

Number of imaginary frequencies = 0

Benzene

C	0.00000	0.00000	1.05445
C	0.00000	-1.21214	1.75429
C	0.00000	-1.21214	3.15396
C	0.00000	0.00000	3.85381
C	0.00000	1.21214	3.15396
C	0.00000	1.21214	1.75429
H	0.00000	0.00000	-0.03413
H	0.00000	-2.15489	1.21001
H	0.00000	-2.15489	3.69825
H	0.00000	0.00000	4.94239
H	0.00000	2.15489	3.69825
H	0.00000	2.15489	1.21001

Energy = −232.145527325 hartree

Number of imaginary frequencies = 0

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6 ^{1}H and ^{13}C{^{1}H} NMR spectra of all new compounds

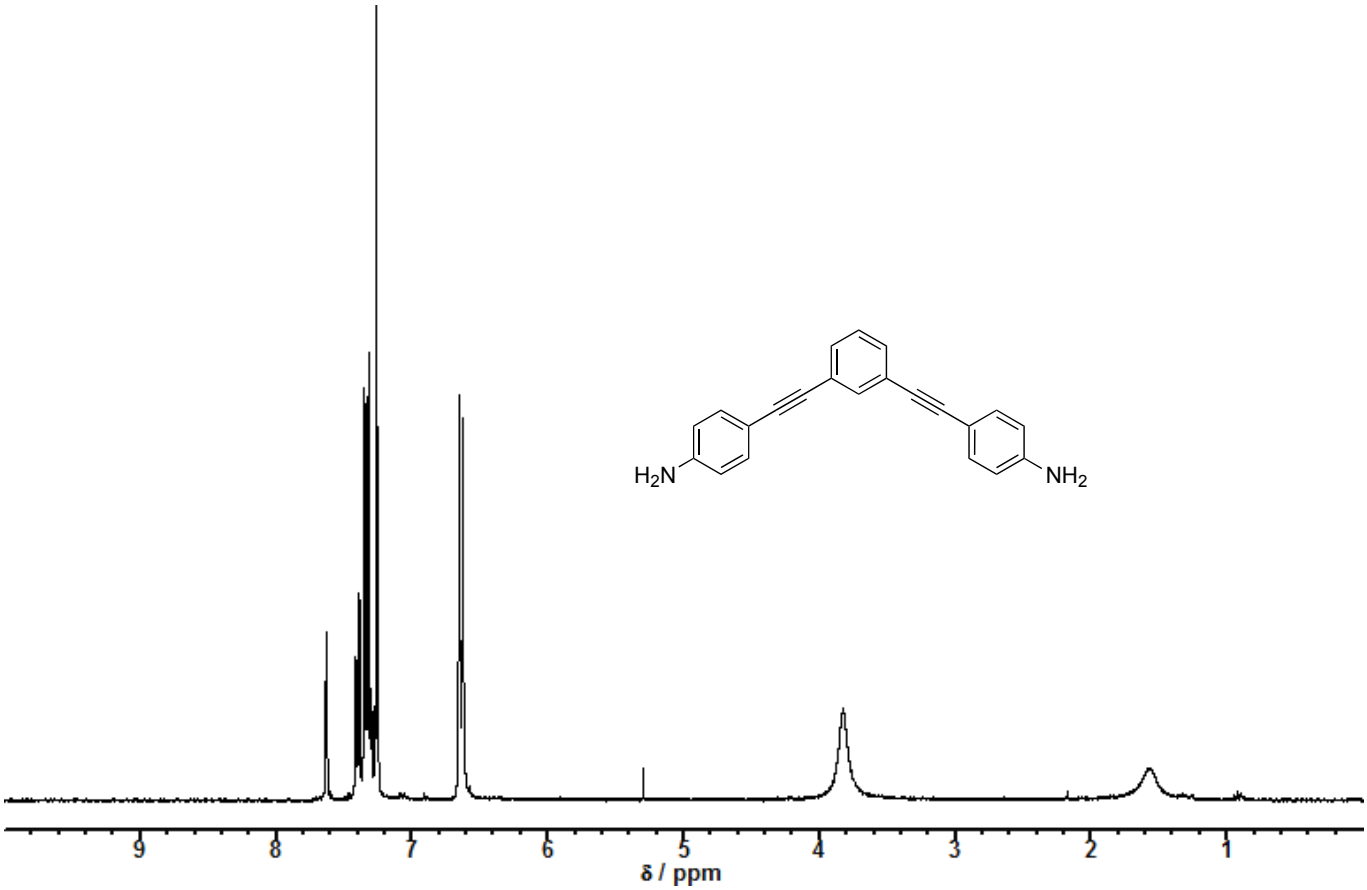

Figure S11. ^{1}H NMR spectrum of 1,3-bis(4-aminophenylethyny)benzene ($CDCl_3$).

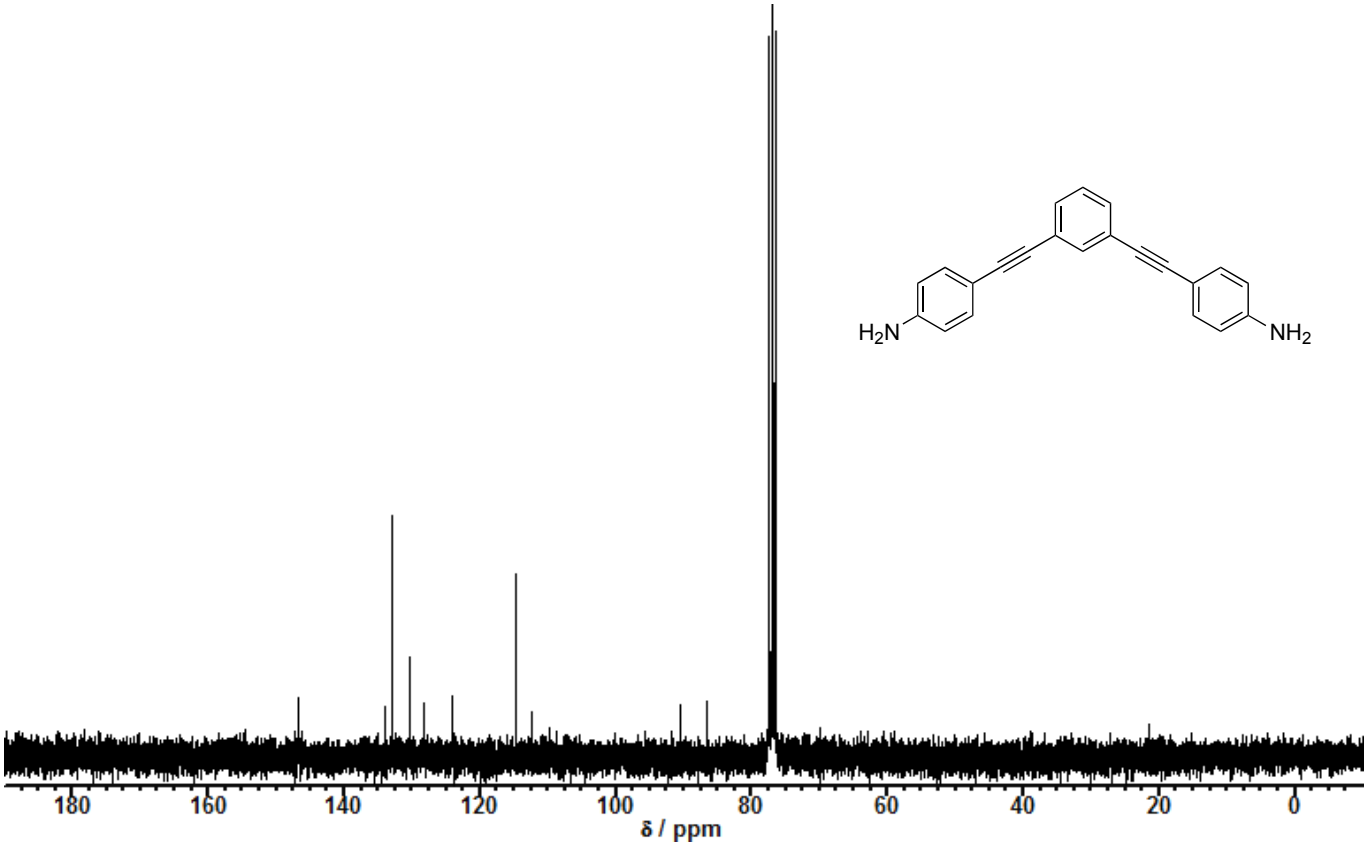

Figure S12. ^{13}C NMR spectrum of 1,3-bis(4-aminophenylethyny)benzene ($CDCl_3$).

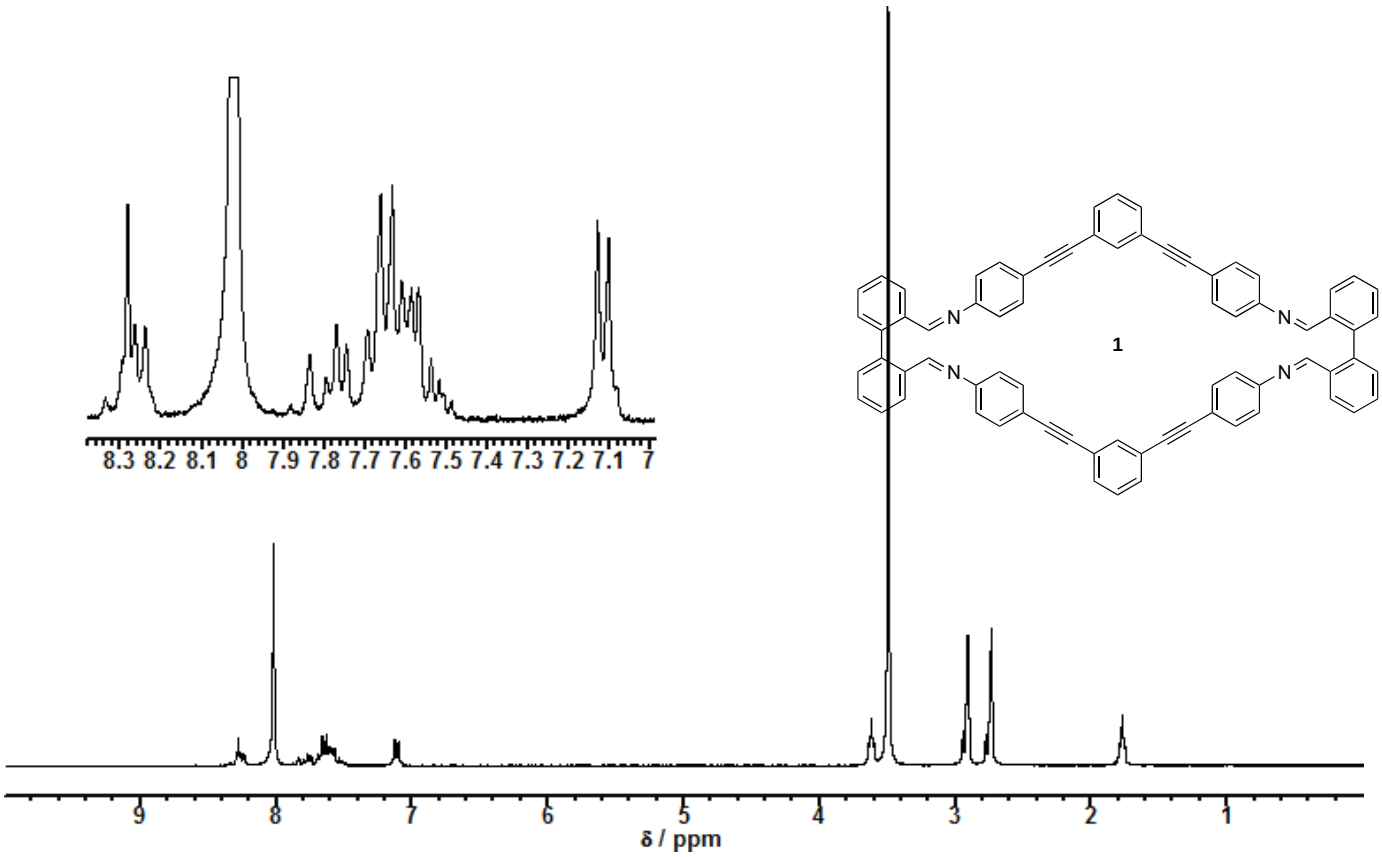

Figure S13. ^{1}H NMR spectrum of **1** (DMF-d_7).

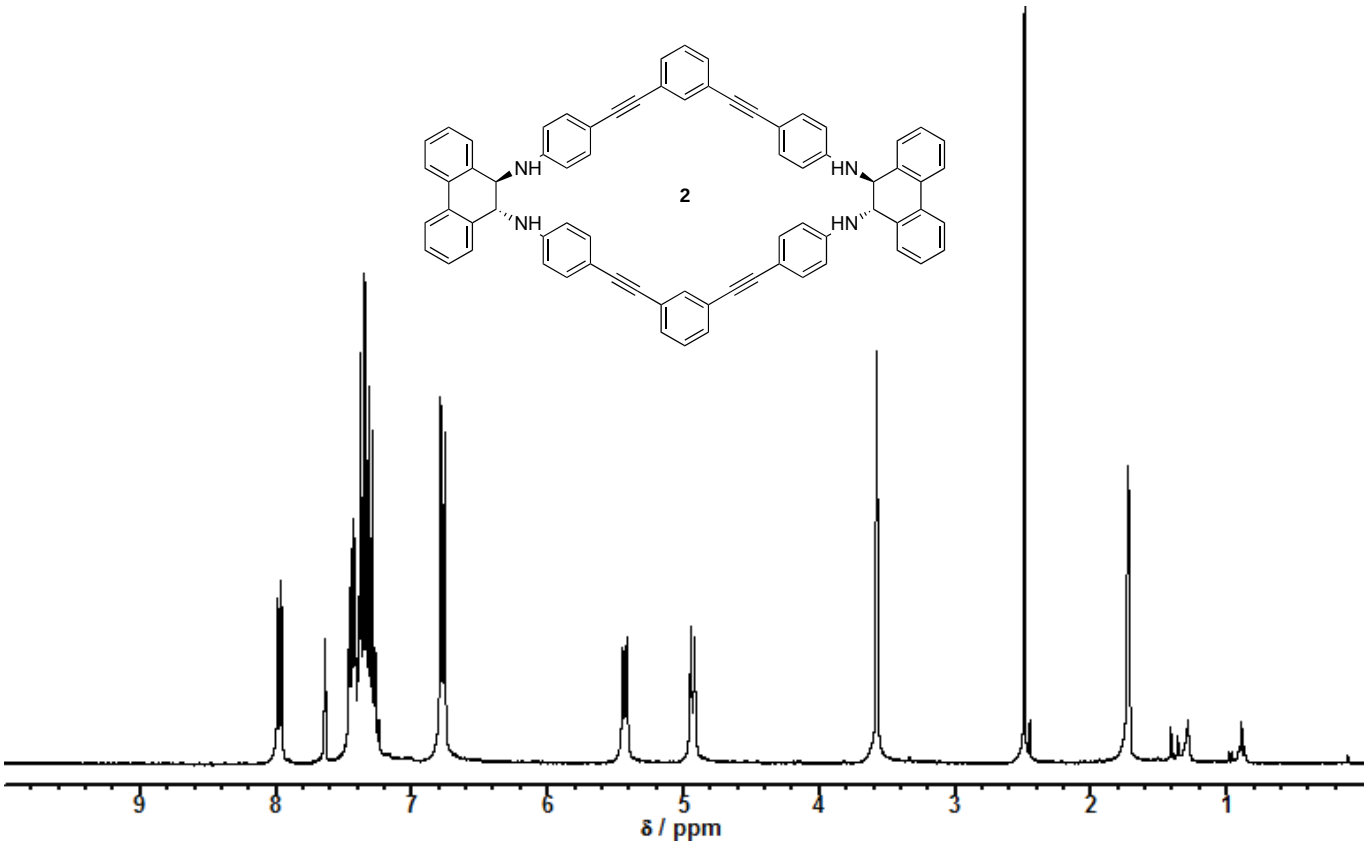

Figure S14. ^{1}H NMR spectrum of **2** (THF-d_8).

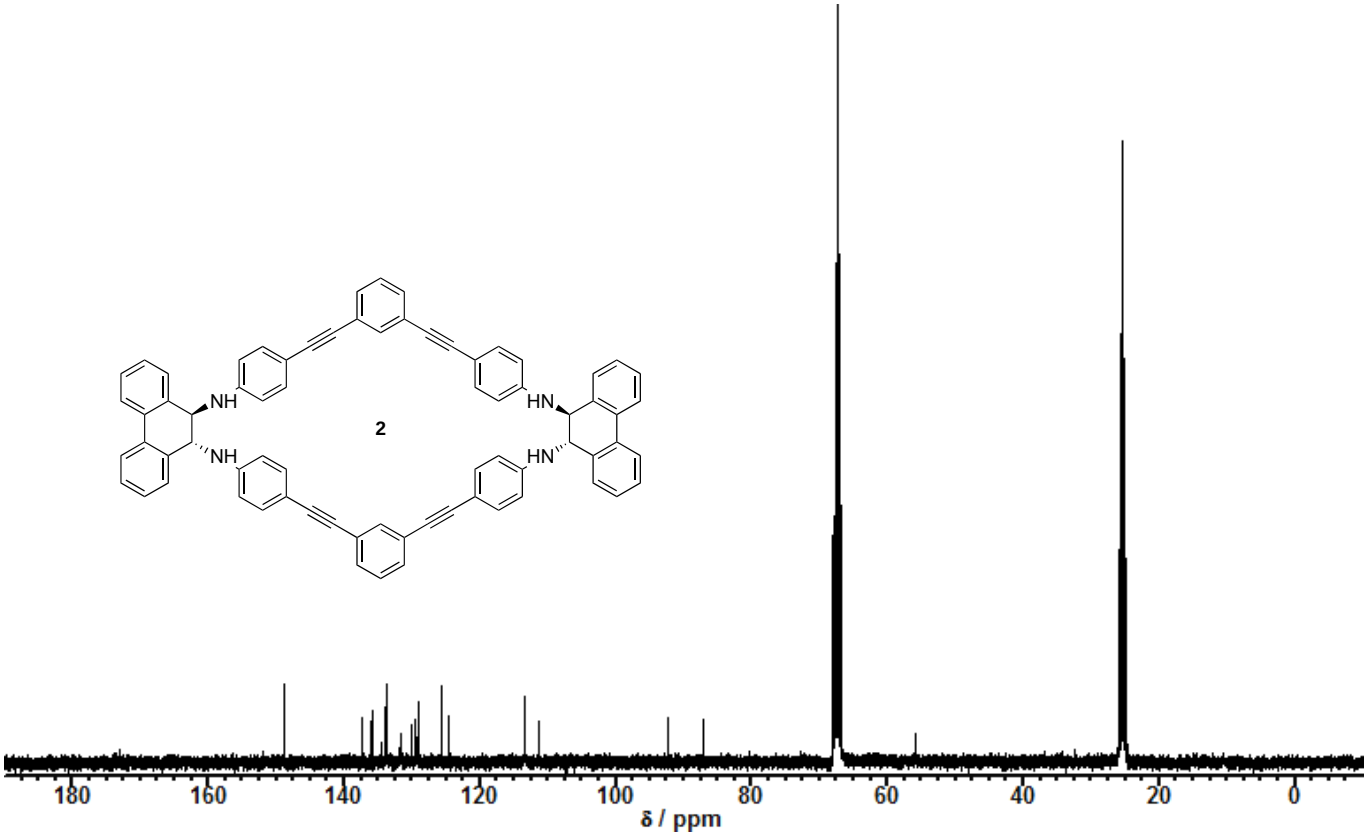

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (THF-d_8).

7 Photophysical properties of 1 and 2

7-1 UV-Vis spectra of saturated solution of 1 and xerogel 1

Saturated solutions of **1** before ultrasound irradiation and xerogel **1** were prepared following procedure. (1) The sample and solvent were taken in test tube and sealed; (2) Stirred by magnetic stirrer for 30 min; (3) Standing overnight. To the measurement of UV-Vis spectrum, the saturated solutions were diluted with solvent 100 times.

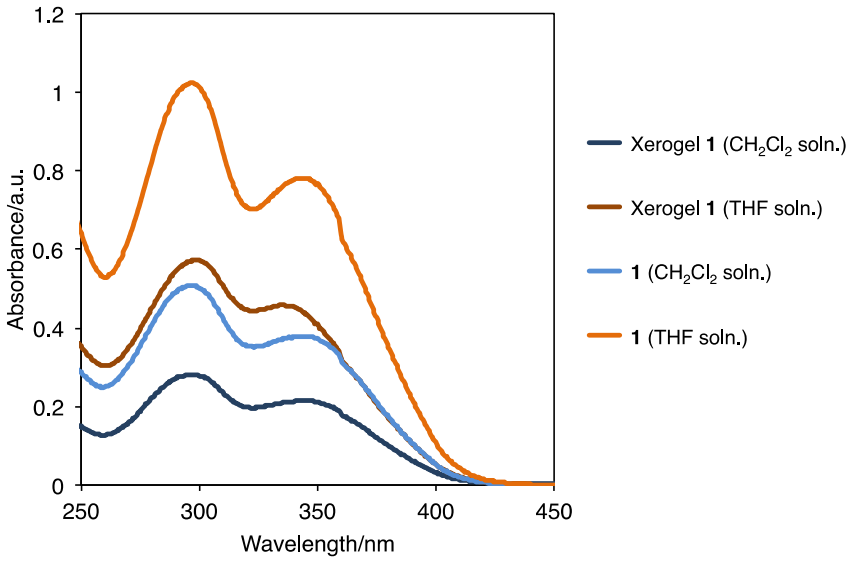

Figure S16. UV-Vis spectra of **1** before ultrasound irradiation and xerogel **1**.

7-2 UV-Vis and fluorescent spectra of 2

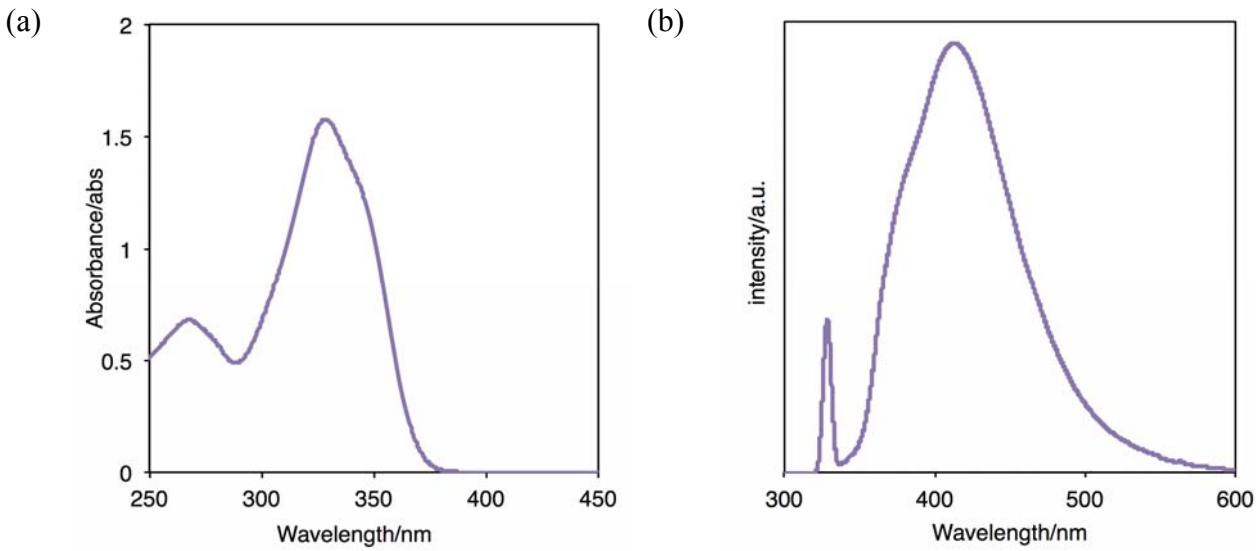

Figure S17. (a) UV-Vis spectra of **2** in 1,4-dioxane (1×10^{-4} M) and (b) Fluorescent spectra of **2** in 1,4-dioxane (1×10^{-5} M).

Table S3. Photophysical properties of **2**.

Compound	λ_{abs}/nm	ε_{max}/M^{-1}□cm^{-1}	λ_{ex}/nm	λ_{em}/nm	Φ_F
2	328	158000	328	413	0.023